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Silahydrocarbons*

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I. INTRODUCTION

Although there are currently no commercial applications for silahydrocarbons, this class of compounds has such unique properties that it remains interesting. The term "silahydrocarbons" is used here to describe a class of compounds mat is more correctly termed tetraalkylsilanes (SiR_4). The alkyl groups on silicon can be the same or different. Additionally, the alkyl groups can be straight-chained (i.e., *n*-alkyl) or branched. For reasons discussed later, the silahydrocarbons of most interest have been those that contain *n*-alkyl groups. In this chapter the term "silahydrocarbon" refers generically to the class of compounds; "tetraalkylsilane" is used as appropriate to clarify discussions of the chemistry.

II. HISTORICAL DEVELOPMENT

While the history of silahydrocarbons goes back well over 100 years, it was in the 1950s that the modern history of their development as functional fluids began. The role of the U.S. Air Force, for the most part, defines that history until the very recent past. The U.S. Air Force Materials Laboratories began a general investigation into the synthesis and properties of tetraalkylsilanes in the 1950s [1–3]. These fluids were called silahydrocarbons [4] to emphasize their hydrocarbon-like behavior. The driving force for the research was the recognition that new high performance aircraft would require lubricants and fluids capable of operating in a high temperature/high load environment. Over the years, the interest in silahydrocarbons rose and fell, finally reaching a peak in the 1980s. During this period, target specifications evolved for candidate fluids for use as hydraulic fluids in high performance aircraft. These target specifications eventually evolved to incorporate the low temperature requirements of MIL-H-5606 (mineral oil) [5] with the high temperature requirements of MIL-H-83282 [synthetic poly(α-olefins),

*This chapter is dedicated to the memory of Gunner E. Nelson.

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Table 1 Original Target Properties of Military Hydraulic Fluids as Derived from MIL-H-83282 and MIL-H-5606

Fluid property	Target	MIL-H-5606	MIL-H-83282
Kinematic viscosity, cSt			
At −54°C, maximum	2500	2500	NA
At −40°C, maximum	500	600	2600
At, 100°C, minimum	3.5	4.9	3.5
Pour point, °C, maximum	−59.4	−60	−55
Shear stability, MIL-H-5606D, % viscosity change	0	0	0
Flash point, °C (open cup), minimum	163	82	205
Fire point, °C, minimum	191	NA	245

PAO] [6]. Table 1, gives a partial listing of these hybrid target properties. Kinematic viscosity and most of the other properties were targeted to those of MIL-H-5606E fluid at low temperature and MIL-H-83282 at high temperature.

The early front-runner was a PAO-based fluid. However, it was recognized that the flash point of this new fluid would be lower than the MIL-H-83282 specification (205°C minimum). The lower flash point was a consequence of the lower molecular weight required to obtain the desired kinematic viscosities at low temperatures. This compromise in flash point, in large part, spurred further development of silahydrocarbons as candidate hydraulic fluids. The inherent chemical structural differences between silahydrocarbons and PAOs made it possible to produce a silahydrocarbon-based fluid with a flash point matching MIL-H-83282 PAO and having the low temperature viscosity of the more volatile mineral oil. The subject of silahydrocarbon properties versus those of hydrocarbons is discussed later. By the late 1970s, the Air Force had successfully developed a silahydrocarbon composition nearly meeting these specifications [7]. It possessed excellent thermal stability, viscosity index, and low temperature flow characteristics. The properties of the Air Force silahydrocarbon fluid are compared to the target properties in Table 2.

III. CHEMISTRY

The literature contains numerous reports on methods of preparation of silahydrocarbons, some dating back over a century. The types of reaction that appear to be useful include alkylation of

Table 2 Silahydrocarbon Performance Versus Target Properties for Low Temperature MIL-H-83282

Fluid property	Determined	Target
Kinematic viscosity, cSt		
At −54°C, maximum	2410	2500 maximum
At −40°C, maximum	564	500 maximum
At, 100°C, minimum	2.58	3.5 minimum
Pour point, °C, maximum	<−65	−59.4 maximum
Shear stability, MIL-H-5606D, % viscosity change	0	0
Flash point, °C (open cup), minimum	227	163 minimum
Fire point, °C, minimum	238	191 minimum

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silicon halides and hydrosilation of olefins. Alkylation can be affected by lithium, magnesium, zinc, and aluminum alkyl compounds. Each of these will be discussed in turn. A note regarding nomenclature is appropriate at this point. The valence of silicon in silane-type compounds is always 4. When naming silanes, it is customary to leave out any hydrogens directly bonded to the silicon. Thus, methyldichlorosilane is CH_3Cl_2SiH.

A. Magnesium

The first synthesis of tetraalkylsilanes (silahydrocarbon), reported by Friedel and Crafts in the raid-1800s [8,9] was the reaction of alkyl magnesium halides (Grignard reagent) with tetrachlorosilane to give low molecular weight symmetrical tetraalkylsilanes such as tetraethylsilane.

$$4RMgX + SiCl_4 \rightarrow R_4Si + 4MgXCl$$

Since then, many workers have studied the preparation of tetraalkylsilanes via magnesium reagents. Gilman and Clark [10] studied the reaction of alkyl magnesium halides with alkyl trichlorosilane.

$$3R'MgX + RSiCl_3 \rightarrow RSiR'_3 + 3MgXCl$$

The air force researchers [4,11] developed a route based on the reaction of mixed alkyl magnesium halides or mixed alkyl lithium reagents with tetrachlorosilane or alkyltrichlorosilane. The case for the mixed magnesium reagent reaction with methyltrichlorosilane is:

$$RBr + R'Br + 2Mg \rightarrow RMgBr + R'MgBr$$

$$CH_3SiCl_3 + 3[RMgBr + R'MgBr] \rightarrow [CH_3SiR_3 + CH_3SiR_2R' + CH_3SiRR'_2 + CH_3SiR'_3] + 3MgBrCl$$

R = *n*-octyl R′ = *n*-decyl

A key to obtaining desirable low temperature properties in the final fluid was the fact that the product was a mixture of compounds similar in molecular weight. Thus suppressed solidification. For the fluid whose properties are reported in Table 2, R and R′ are 50:50 mixtures of *n*-octyl and *n*-decyl.

Lennon at Monsanto developed two routes to methyltrialkylsilanes based on the catalyzed reaction of dialkyl magnesium with methyltrichlorosilane [12–14]. The preparation of magnesium hydride and its subsequent reaction with α-olefins to give dialkyl magnesium was previously known [15].

$$Mg + H_2 \rightarrow MgH_2$$

$$MgH_2 + \alpha\text{-olefin} \rightarrow MgR_2$$

$$3MgR_2 + 2CH_3SiCl_3 \xrightarrow{cat} 2CH_3SiR_3 + 3MgCl_2$$

Both cyanide compounds, such as cuprous cyanide [12], and thiocyanate salts [13] are used as catalysts. With either class of catalyst, Grignard reagents may take the place of the dialkyl magnesium. If a mixture of α-olefins is used a mixture of products, such as that described by she Air Force researchers, results.

B. Lithium

Prior to the work by the Air Force discussed above, where an alkyl lithium was shown to be able the place of an alkyl magnesium halide [10], Gruttner and Wiernik reported the reaction

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of an alkyl lithium with a trialkyisilane to give the first unsymmetrically substituted tetraalkylsilane [16].

$$R'Li + R_3SiH \rightarrow R_3SiR' + LiH$$

Gilman and Massie reported the reaction of alkyl lithiums with tetrachlorosilane to give symmetrical tetraalkylsilanes [17]:

$$4RLi + SiCl_4 \rightarrow R_4Si + 4LiCl$$

C. Zinc

There is a report by Bygden [18] of the reaction of dialkyl zinc with tetrachlorosilane to give symmetrical tetraalkylsilanes:

$$2ZnR_2 + SiCl_4 \rightarrow R_4Si + 2ZnCl_2$$

D. Aluminum

Jenkner's route [19,20] involves the reaction of trialkyl aluminum with methyltrichlorosilane catalyzed by a metal chloride to give low molecular weight tetraalkylsilanes:

$$CH_3SiCl_3 + AlR_3 + MCl \rightarrow CH_3SiR_3 + MAlCl_4$$
$$R = CH_3 \text{ or } CH_3CH_2$$

Bakshi et al. [21] later developed a similar route that gave high molecular weight products. For example:

$$CH_3SiCl_3 + Al(C_8H_{17})_3 + NaCl \rightarrow CH_3Si(C_8H_{17})_3 + NaAlCl_4$$

Depending on the exact conditions, various levels of tetra-*n*-octylsilane and dimethyl-di-*n*-octyl silane could be produced as coproducts. The use of 0.5 equiv of sodium chloride based on the tri-*n*-octyl aluminum was found to maximize the yield of the desired product, methyl-tri-*n*-octyl silane.

Nelson and coworkers at Ethyl developed a route to tetraalkylsilanes based on the alkylation of chlorosilanes with sodium aluminum tetraalkylates [22–26]. The route involves first the preparation of the sodium aluminum tetraalkylate via the reaction of sodium aluminum hydride with α-olefins. The intermediate tetraalkylate is next used to alkylate a chlorosilane, such as methyltrichlorosilane:

$$NaAlH_4 + 4(C_8/C_{10}\ \alpha\text{-olefin}) \rightarrow NaAl(C_8H_{17})_x(C_{10}H_{21})_{4-x}$$
$$3NaAlR_4 + 4CH_3SiCl_3 \rightarrow 4CH_3SiR_3 + 3NaAlCl_4$$

The product is a mixture of the four components described by the Air Force workers. Adjusting the C_8/C_{10} olefin ratio can readily alter product distribution, or, if another composition is required, olefins of other carbon numbers can be used. In an interesting modification of this process, olefin/aluminate interchange is used:

$$NaAlR_4 + 4(C_8\ \alpha\text{-olefin}) \rightarrow NaAl(C_8H_{17})_4$$
$$NaAl(C_8H_{17})_4 + C_{10}\ \alpha\text{-olefin} + 4CH_3SiCl_3 \rightarrow 4CH_3Si(C_8H_{17})_x(C_{10}H_{21})_{3-x} + NaAlCl_4$$

Presumably, a rapid exchange of alkyl groups on the aluminate occurs during the alkylation process, yielding again the four-component mixture, with the relative mole fractions of each calculable on the basis of the C_8/C_{10} ratio as before. Such chemistry can be used to produce phenylalkylsilanes [27,28]. A similar route involves the treatment of a trialkyl aluminum with

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sodium followed by reaction with methyltrichlorosilane [29]. In an interesting extension of this chemistry, the sodium aluminum tetraalkylate can be prepared directly from sodium, aluminum, hydrogen, and α-olefins. This reaction product can then be reacted with a methyltrihalosilane [30].

Researchers at Shin-Etsu [31] reported the preparation of low molecular weight silahydrocarbons via the reaction of chlorosilanes with chlorinated hydrocarbons in the presence of metallic aluminum or aluminum alloys. A similar route was reported by researchers at Dow Coming [32].

E. Hydrosilation

Hydrosilation has also been utilized in the preparation of tetraalkylsilanes. While it is likely not of preparatory significance, Austin et al. [33] reported an interesting route to tetraalkylsilanes. These investigators studied the photocatalyzed reaction of alkenes with alkylsilanes using trinuclear metal carbonyl catalyst precursors. Thus, irradiation of $M_3(CO)_2$ (M = Fe, Ru, or Os) in the presence of 1-pentene and $HSiEt_3$ gave n-$C_5H_{11}SiEt_3$,

El-Durini and Jackson [34] studied another interesting approach. They reported the reaction of tripropylsilane with 1-octene in the presence of a free radical initiator. When the starting silane was present in excess, a high yield of the product, octyltripropylsilane, was obtained.

Onopchenko and Sabourin [35,36] developed a route based on catalytic hydrosilation of α-olefins by mono-, di-, or trialkylsilane. Various platinum-based catalysts are claimed. For example,

$$(C_8\ \alpha\text{-olefin}) + C_6H_{13}SiH_3 + H_2PtCl_6 \cdot 6H_2O \rightarrow (C_8H_{17})_3(C_6H_{13})Si$$

A key to high conversion to the tetraalkylsilane is the exposure of the catalyst to oxygen. Under similar conditions, using a rhodium-based catalyst, the inventors were able to prepare mixtures of tetraalkylsilane that contained various levels of unsaturation in the side chains [37]. The mixture can be hydrogenated to provide a saturated tetraalkylsilane. The unsaturation can also be sulfurized to provide a compound that can act as a lubrication additive.

Onopchenko and Sabourin [38] developed another route to tetraalkylsilanes based on hydrosilation of α-olefins. The scheme involves hydrosilation of an α-olefin by methyldichlorosilane followed by reduction of the resultant methylalkyldichlorosilane to the methylalkylsilane by lithium aluminum hydride. This product is, in turn, reacted with another α-olefin via catalytic hydrosilation. This reaction scheme allows the synthesis of a series of methyldialkylalkylsilanes:

$$CH_3SiCl_2H + \alpha\text{-olefin} + \text{catalyst} \rightarrow CH_3SiCl_2R$$
$$CH_3SiCl_2R + LiAlH_4 \rightarrow 2CH_3SiH_2R + LiAlCl_4$$
$$CH_3SiH_2R + \alpha\text{-olefin} + \text{catalyst} \rightarrow CH_3SiR'_2R$$

Malcolm et al. [26,39] developed a route to silahydrocarbons starting from silane (SiH_4) itself. This route involves the partial alkylation of silane by sodium aluminum tetraalkylate. The olefin employed in the last step can be ethylene. The resulting product would thus be an ethyltrialkysilane, in contrast to the methyltrialkysilane produced by the methods starting from methyltrichlorsilane:

$$SiH_4 + NaAlR_4 \rightarrow R_2SiH_2 + R_3SiH$$
$$R_2SiH_2 + R_3SiH + Co_2(CO_8) \rightarrow R_3SiH$$
$$R_3SiH + \alpha\text{-olefin}' + \text{catalyst} \rightarrow R_3SiR'$$

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More recently, LaPointe et al. [40] reported studies of the palladium-catalyzed hydrosilation of alkenes by either triethyl- or triphenylsilane (R_3SiH).

IV. PERFORMANCE

As mentioned earlier, the term "silahydrocarbon" was chosen to describe the class of compounds under discussion because of their hydrocarbon-like character. Indeed, in many ways they are similar to hydrocarbons. It has been shown that silahydrocarbons are compatible with mineral oils and PAOs [38]. This compatibility is one aspect of the fluids that made them attractive to the air force as drain-and-fill replacements for existing hydraulic fluids. There are, however, some inherent differences, and these form the basis for the interest in these materials. Most of the work on the properties of silahydrocarbons centers on their potential as hydraulic fluids. Therefore a property-by-property comparison to mineral oil and PAOs is warranted. Chapter 18 contains a more general discussion of the properties of a wider variety of fluids.

A. Viscosity

As seen in the discussion of the chemistry, it is possible to synthesize a large number of tetraalkylsilanes of the type SiR_4. Since R can be any hydrocarbon group from one carbon up, an enormous number of possibilities exist. A good starting point in understanding the difference between silahydrocarbons and hydrocarbons is a review of physical properties of compounds with similar structures. The melting points of several tetraalkylmethanes and tetraalkylsilanes are shown in Table 3. From the data, it is clear that for a given structure, the substitution of silicon for the quatenary carbon lowers the melting point dramatically. In practice, this translates to a beneficial decrease in pour point for fluids of similar molecular weight.

There are reports in the literature of the synthesis of silahydrocarbons over a wide range of molecular weights [3,26,38,39,41]. A review of the data shows that the viscosity is a linear function of the molecular weight and is not influenced greatly by the molecular structure [42]. The linearity of the relationship is particularly impressive considering that some of the fluids are pure compounds and some are mixtures. Also, the fluids are composed of four classes of tetraalkylsilanes: dodecyltrialkysilanes, didodecyldialkylsilanes, methyltrialkylsilanes, and ethyltriakylsilanes. It is important to note that the viscosity correlation does not necessarily translate to low temperature. As the temperature is lowered, the fluids comprising single corn-

Table 3 Comparison of Melting Points of Silicon and Carbon Analogues

Carbon analogue	Melting point (°C)	Silicon analogue	Melting point (°C)
$(CH_3)_4C$	−16	$(CH_3)_4Si$	−95
$(CH_3CH_2)_4C$	−31	$(CH_3CH_2)_4Si$	−69
$(n\text{-}C_3H_7)_4C$	−26	$(n\text{-}C_3H_7)_4C$	−46
$(n\text{-}C_4H_9)_4C$	−6	$(n\text{-}C_4H_9)_4C$	−46
$(n\text{-}C_4H_9)_3C(CH_2CH_3)$	−66	$(n\text{-}C_4H_9)_3Si(CH_2CH_3)$	−91
$(n\text{-}C_4H_9)_3C(CH_6CH_{13})$	−51	$(n\text{-}C_4H_9)_3Si(CH_6CH_{13})$	−72

Source: Ref. 4.

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pounds suffer from the problem of crystallization (i.e., freezing]. A fluid that is a mixture of compounds of similar but different molecular weights will have a pour point below that at which the single-component fluid would solidify.

A discussion of viscosity is not complete without taking viscosity index and pour point into account. The viscosity indices of a mineral oil, a PAO, and a silahydrocarbon of the same 100°C viscosity are 94, 127, and 151, respectively [43]. A high viscosity index is favorable, indicating that the viscosity does not show large variations with temperature. The pour point of the mineral oil is only −15°C while both the PAO and silahydrocarbon pour points are below −65°C.

B. Lubricity

Silahydrocarbons were recently compared to a mineral oil and a PAO [43]. In the absence of additives, the lubricity of the mineral oil was found to be slightly better than that of the PAO, as measured by the size of me wear scar in the four-ball wear test. Both were better than the silahydrocarbon. In the presence of 1% antioxidant and 3% of an antiwear additive, the mineral oil and PAO were equivalent, and both were better than the silahydrocarbon. It is significant that the additives improved the performance of the silahydrocarbon, because this is not the case for some classes of fluids. It may be that an additive package developed specifically for silahydrocarbons would give better performance. Earlier work by the Air Force showed that the lubricities of the three fluids were equivalent in the presence of an antioxidant and an antiwear additive [44].

C. Thermal Stability

The Air Force researchers reported the results of a systematic investigation into the relative performance of silahydrocarbons and several other candidate fluids as high temperature lubricants [44]. In regard to thermal stability, they found that silahydrocarbons were inherently more stable than mineral oil or PAO. Later work by researchers at Ethyl confirmed this finding [42]. This difference in thermal stability is likely due to the different amounts of branching in the structures. The silahydrocarbon has the advantage of having a well-controlled structure with no branching other than the quaternary branch centered at silicon. It is well established that both mineral oils and PAOs used as hydraulic fluids contain considerable amounts of secondary and tertiary branch points. It has been argued that hydrocarbons of the same structure should be no less thermally stable than a given silahydrocarbon, provided both materials are pure [45]. Other work has shown that the situation may be more complex. Researchers at Chevron found, as expected, that incorporation of tertiary hydrogen near the end of an alkyl chain in a silahydrocarbon decreased the thermal stability [38]. However, incorporation of tertiary hydrogen on the carbon alpha to the silicon actually made the molecule more stable. Researchers at Pennzoil found that synthesized tetra(*n*-alkyl)methanes and tri(*n*-alkyl)methylmethanes exhibited a good balance of properties compared to PAOs and tri(*n*-alkyl)methylsilanes [46].

D. Oxidative Stability

Results cited by both the Air Force [43] and Ethyl [47] show that formulated silahydrocarbons and PAOs are equivalent in oxidative stability and that both are clearly superior to mineral oils. In further work the Air Force researchers studied the affect of side chain structure on the oxidative stability of a series of alkyltrioctylsilanes [48].

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Table 4

Sources of Silahydrocarbons	
Huls America	80 Centennial Avenue P.O. Box 456, Piscataway, NJ 08855-0456 Tel: 908-980-6940 Fax: 908-560-6800 *http://www.huls.com*
Lancaster Synthesis Ltd.	P.O. Box 1000 Windham, NH 03087-9777 Tel: 603-889-3306 Fax: 603-889-3326 *http://www.lancaster.co.uk*
Aldrich Chemical Company, Inc.	940 West Saint Paul Avenue Milwaukee, WI 53233 Tel: 414-273-3850 Fax: 414-273-4979, *http://www.aldrich.sial.com/aldrich.html*

E. Hydrolytic Stability

The hydrolytic stability of silahydrocarbons, silicate esters, and polysiloxanes was evaluated with regard to the possible use as dielectric coolants in military aircraft [49]. These studies showed silahydrocarbons to be resistant to hydrolysis.

F. Volatility and Flammability

The volatility of nonpolar compounds is a function of molecular weight, as is the viscosity. A silahydrocarbon, mineral oil, and a PAO of the same viscosity at 100°C were measured by thermogravimetric analysis to determine their volatilities [42]. The temperature required to induce 5, 50, and 95% weight loss is cited for each fluid. These data clearly show that the silahydrocarbon is the least volatile. This difference in volatility translates to higher flash point as measure by ASTM D-92. The flash points are: silahydrocarbon, 234°C; PAO; 218°C; and mineral oil, 197°C.

G. Summary of Properties

The key features of silahydrocarbons are low temperature fluidity, high thermal stability, low volatility (hence high flash point), and high viscosity index. In comparison to PAOs, the superior thermal stability, high viscosity index, and low volatility (high flash point) seem to be the advantages that would lead one to consider a silahydrocarbon as a candidate fluid.

V. COMMERCIAL STATUS

At present, there is no readily available information that indicates significant commercial applications for silahydrocarbons [50,51]. The patent literature discloses few uses for silahydrocarbons outside the hydraulic area. Milliken Research [52] and Ethyl Corporation [53] patented the use of silahydrocarbons as textile finish lubricants. Ferrofluidics [54,55] developed the use of silahydrocarbons in ferrofluid applications. Nippon Polyurethane [56] discloses the use of

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tetraoctadecylsilane as an internal mold release agent in the manufacture of polyurethane and polyurea articles. Several pure, low molecular weight tetraalkylsilanes are available from chemical supply companies. Some of these companies are listed in the appendix.

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